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Molecular relaxation effects on hydrogen chloride photoacoustic detection

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Photoacoustic spectroscopy (PAS) is a widely recognized method for its high performances in trace gas measurements. This technique provides many advantages such as a high selectivity and sensitivity, on-line, real time and contactless measurements in a compact experimental arrangement. It is based on the periodic absorption of a modulated laser beam tuned to an absorption line of the gas to be detected, so that the absorbed energy induces a periodic heating in the sample and an acoustic wave is generated through normal thermal expansion. Molecular relaxation of the rovibrational energy into sample heating is a key step in the generation of the photoacoustic (PA) signal. This effect is assumed to be instantaneous in most of the cases, since it is much faster than the time scale of the laser modulation. However, in some particular gas mixtures, it turns out that this relaxation is much slower and thus strongly influences the generation of the PA signal.

In this work, we present relaxation effects occurring in hydrogen chloride (HCl) detection at sub-ppm level using a near-infrared laser diode emitting at 1738 nm. The influence of a gas mixture composed of helium (He) and nitrogen (N_2) on the PA signal was first investigated. A decrease of the sensor sensitivity of about 50% was observed when 10% of N_2 was added to the gas mixture, due to the vibration-to-vibration (V-V) energy transfer that occurs as a result of HCl-N_2 collisions and the long relaxation time of the excited N_2 (ν=1) state. A second gas mixture, composed of He and oxygen (O_2) was studied to compare the relaxation effects on the PA signal. V-V energy transfer due to HCl-O_2 collisions also occurs which lead to a partial transfer of energy to the O_2 (ν=1) excited state, which also presents a long relaxation time. However, the relaxation effects in this second gas mixture were more complex, since it was observed that He acted as a catalyst on the HCl-O_2 gas mixture, thus strongly modifying the sensor response. Molecular relaxation effects are explained by considering the deactivation pathway of the excited HCl molecules, based on the energy diagrams of the different molecules involved in the process and a qualitative model is presented. In addition, the role of water vapor (H_2O) acting as a catalyst in the HCl-N_2-He and HCl-O_2-He systems was also clarified. It was observed that about 0.5% of H_2O in the HCl-O_2-He gas mixture and 0.8% in the HCl-N_2-He system were sufficient to retrieve the maximum of the PA signal.